The Analysis of Gases after Passage of Electric Discharge.

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Introduction.

It has been found by Collie and Patterson* that, after the passage of the electric discharge through pure hydrogen in a vacuum tube at low pressure, small quantities of helium and neon could be detected in the gas pumped out of the discharge tube. These gases were shown not to be present in the hydrogen which was let into the discharge tube. They must, then, either originate from—(i) occlusion of air in the glass or electrodes, or (ii) from the outer air during the experiment or the subsequent analysis, or (iii) be actually formed by some transmutation process due to the action of the discharge. In the latter case the seat of the effect of the discharge may be at the solid electrode, glass walls, or in the gas itself. The experiments of the above authors appear to show that:—

(i) The gas did not originate from occlusion in the electrodes or glass walls, because these gave no such rare gases on solution and subsequent analysis of the gases.

(ii) The gases did not enter from the outer air, because similar effects were obtained when the tube was jacketed by another tube, the space between the two being evacuated. Sometimes, also, only helium was obtained, whereas neon would be expected if air had leaked in.

(iii) The gas was not formed by some change at the electrodes, as similar effects were obtained (though to a lesser extent) by means of an electrodeless discharge.

The result of the work indicated, then, that the hydrogen (or possibly the glass tube) had in some way been affected by the discharge, so as to obtain helium or neon. It is noteworthy that positive results of the production of He or Ne are only sometimes obtained. J. J. Thomson† had noticed that helium lines were always very marked in the positive ray spectrum produced during the bombardment of metallic substances by cathode rays, when only pure hydrogen had been allowed to enter the discharge tube. He favoured the view that the metallic electrodes were responsible for the production of the helium, and that it might have been formed by slow radioactive processes and only liberated by the cathodic bombardment. Subsequently the Hon. R.

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* 'Chem. Soc. Trans.,' vol. 103, p. 419 ; and 'Chem. Soc. Proc.,' vol. 29, p. 217 (1913).

† 'Nature,' vol. 90, p. 645 (1913).

Strutt made a short investigation of the subject,* but obtained no trace of helium or neon in the gas, which was analysed after passage of the discharge. He further showed that a minute quantity of air could be detected by means of the residual neon (after getting rid of hydrogen by sparking with oxygen, and absorbing the residual gas by means of cooled charcoal). He held that the gases could not be safely transferred by means of small inverted tubes over mercury, without the possibility of a trace of air entering during the process: and this led him to construct an apparatus which was entirely self-contained, and by means of which all external transference from the discharge tube to the analysis apparatus was entirely avoided.

The work of these investigators has not, therefore, led to similar results, and the following questions present themselves:—Firstly, were the electrical conditions of Strutt's experiments unfavourable to the formation of rare gases? Secondly, was the method of analysis less sensitive? Thirdly, is it possible to prevent access of air into the apparatus during the experiment and analysis, and to entirely free the electrodes of all detectable traces of rare gases?

In the work to be described, which was carried out in continuation of some other work along similar lines, special attention has been paid to these points: the electrical conditions were varied considerably by altering the generating apparatus and the shape of the discharge tubes; the method of analysis was made as sensitive as possible and blank tests were frequently applied. The result, unfortunately, has not thrown any light on the production of the rare gases, as these gases were not obtained when the tube and electrodes had been evacuated as far as possible, and when there was no detectable leakage of air in the apparatus.

Experimental.

In continuation of some former work the apparatus depicted was built. It has been found that when the gases were pumped out of the discharge tube and transferred by means of small tubes to the analysing burettes, as often as not, traces of argon could be detected. This argon was traced to some mercury; by means of tube D, this difficulty was overcome and the gases could be brought directly and completely into the analysing burette from the discharge tube without coming into contact with mercury, which stands in the presence of air. The presence of about of 0·1 cu. mm. of air can be detected by the argon. The nitrogen is often not found unless larger quantities of air are present, as ozone is formed during the analysis and combines with the nitrogen and mercury; phosphorus, too, absorbs small quantities of nitrogen. Neon was only found when much larger quantities of air were present.

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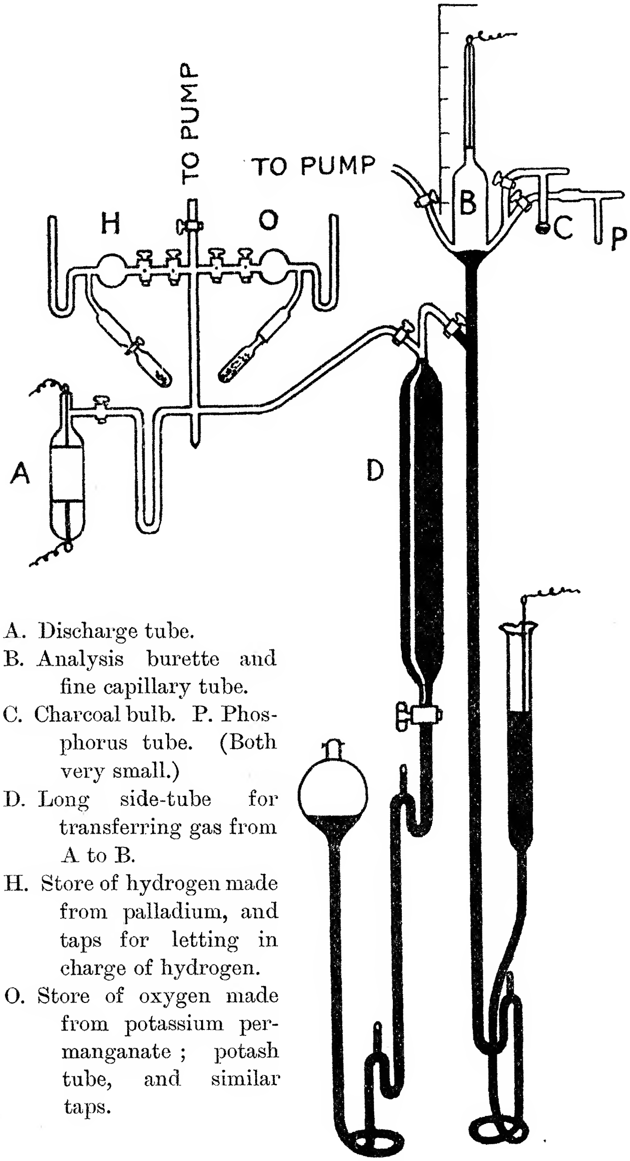
* 'Roy. Soc. Proc.,' A, vol. 89, p. 499 (1914).

For the analysis of the gas oxygen is added, the burette is jacketed with a small cup of liquid air, and the discharge is passed; water and ozone are formed and a high vacuum is obtained (ozone partly condensing and partly combining with the mercury). The tube and the mercury are then warmed and oxygen absorbed by opening to the phosphorus or charcoal. Sometimes



A. Discharge tube.
B. Analysis burette and fine capillary tube.
C. Charcoal bulb. P. Phosphorus tube. (Both very small.)
D. Long side-tube for transferring gas from A to B.
H. Store of hydrogen made from palladium, and taps for letting in charge of hydrogen.
O. Store of oxygen made from potassium permanganate; potash tube, and similar taps.

a small quantity of oxygen and carbon oxides remain unabsorbed, these disappear on passing the discharge through the capillary jacketed by liquid air, owing to the formation of ozone; any small residual quantities of nitrogen or of hydrogen also disappear owing to this. In order to be sure that none of the rare gases are hidden, the mercury is warmed, the process of analysis repeated, and the spectrum of the residual gases carefully examined. In the final experiment the hydrogen and oxygen were sparked at ordinary pressure by means of two platinum wires sealed in the burette.

The following experiments are some of those that have been made with this apparatus :—

(*a*) The discharge tube was a cylindrical tube with two disc electrodes placed opposite each other. A 6-inch coil with hammer break was used. Gas analysed by phosphorus—No Ne or He found.

(*b*) Another similar tube. A 9-inch coil with a long spring hammer break. Gas analysed by phosphorus—No A, no He, no Ne found.

(*c*) A similar tube but with both anti-cathode and anode. A large 20-inch coil, Caldwell electrolytic break, plate and point rectifier in the circuit. Gas analysed similarly—Trace A, no Ne, no He. (This merest trace of argon came from the oxygen used for the analysis.)

(*d*) A tube with large spiral aluminium wire as cathode, anode in a small side bulb connected with the narrow tube, the tube acting in some measure as a rectifier. A 20-inch coil, electrolytic break and rectifier, also a 9-inch coil and two types of hammer break. Analysed by charcoal—No Ne or He (experiment lasted 22 hours).

(*e*) A tube with two platinum electrodes ½ cm. by 2 mm. in two glass bulbs (4 cm.) connected by a narrow tube. Gas analysed by charcoal :—

1. A 9-inch coil, hammer breaks and rectifier—No Ne or He.
2. A 20-inch coil, hammer break in series—No Ne or He.
3. A 20-inch coil, electrolytic break and rectifier—No Ne or He.

In this experiment there was much "splashing" from the cathode; in the last part of the experiment the cathode was often bright red hot.

(*f*) Similar tube, aluminium anodes, platinum cathodes. A 20-inch coil, electrolytic break and rectifier. Very much "splashing." Gas analysed by charcoal—No Ne or He.

(*g*) Spectrum-shaped tube; palladium rod anode, palladium plate cathodes, a 9-inch coil and a hammer break. There was so much "splashing" that a larger coil could not be used. Gas analysed by charcoal—No Ne or He.

(*h*) One cubic centimetre was pumped out of a large Röntgen tube, through which the heaviest obtainable unidirectional discharge had been passed for four hours (5 milliampères, between 60,000 and 120,000 volts)—No Ne or He was detected.

In another experiment a little argon was detected, but no Ne or He. A third quantity, which was known to be contaminated by air, was analysed by charcoal and gave a considerable quantity of neon. (I have to thank Dr. Lindemann for these samples of gas.)

(*i*) A spectrum tube with fine platinum wire cathode, a 9-inch coil, hammer break and rectifier. Analysed by phosphorus—No Ne or He, a trace of argon (due to oxygen).

(*j*) A spectrum tube with small bead of platinum as cathode.

1. A 9-inch coil and rectifier (six hours). Analysed by sparking in burette and phosphorus—No Ne or He.

2. A 20-inch coil, electrolytic break and rectifier (five hours, cathode becoming white hot at times). Both together analysed by phosphorus and afterwards by charcoal—A trace of He possibly, but such a small quantity that its presence was doubtful.

In all these experiments the tube was as strongly heated as possible when pumping out the gases, also during the preliminary exhaustion. The discharge was reversed occasionally, as it has been found that a cool anode will often absorb gas given off by a hot cathode. The tube was finally washed out with pure hydrogen. The duration of each experiment was about eight hours, unless otherwise stated. At a certain stage of exhaustion the hydrogen is shot very easily into the walls of the tube, provided the latter does not become too hot or the vacuum too low. Charges of hydrogen are let in, when necessary, from the place between the two taps provided for that purpose. The amount of hydrogen absorbed by the walls appears to depend on the temperature, the shape of the tube, the pressure of the gas, and the potential of the cathode during exhaustion. A long time is required to entirely rid the walls and electrodes of gases; if a stronger cathode discharge is passed through the tube it is generally possible to obtain more gas (hydrogen and a little oxygen). However, with small tubes and many washes with pure hydrogen, it is certainly quite possible to get rid of all detectable traces of air. Once, when a minute leak was present, it was noticed that the spectrum of nitrogen was not given for some minutes, but only that of oxygen; the tube had palladium electrodes. It would seem that very small quantities of nitrogen had been made active, and were absorbed by the metal deposited on the walls of the tube.

Summary of Experiments.—In the above experiments electric discharge has been passed with three different-sized coils, three different types of interrupters, through various sized and shaped tubes, with palladium, platinum, and aluminium electrodes of various shapes and sizes, the analyses of the residual gases being carried out by phosphorus and charcoal in various ways, but no change of the gases, such as the production of helium or neon, has disclosed itself.

Theoretical.

It will be interesting to enquire into the mechanism which could, perhaps, give rise to such a production of helium by means of the electric discharge, and to calculate approximately the amount of energy that would be needed. In the first place, suppose one assumes an association process, and let the helium be formed from a certain quantity of hydrogen. It is a consequence of relativity theory that the variation of the mass of a system is connected with the variation of the internal energy by the following:—

$$\Delta E = c^2 \Delta m \left(\frac{1}{\sqrt{(1-\beta^2)}} - 1 \right),$$

where c^2 is the square of the velocity of light, and the last term merely depends on the movement of the system relative to the observer, and can be neglected in this case.*

$$\therefore \quad \Delta E = 9 \times 10^{20} (4H - He) = 9 \times 10^{20} (4{\cdot}032 - 3{\cdot}99)$$

$$= 3{\cdot}6 \times 10^{19} \text{ ergs per gramme-molecule of helium formed, } i.e.$$

$$6 \times 10^{-5} \text{ ergs per atom of helium.}$$

Every 1/100 cu. mm. of helium formed (a detectable quantity) would therefore need $1{\cdot}6 \times 10^{10}$ ergs. An induction coil certainly might supply this total energy in an hour, but there are two important considerations. First, the energy is only conveyed in the form of charged particles, and there can hardly be particles possessing energy of the order of 10^{-5} ergs within a discharge tube; the energy of the hydrogen ion in the dark space being of the order 10^{-10} ergs, and that of the cathode particles on the average 10^{-9} ergs, (a cathode particle would have to move in a field of over 30 million volts to possess energy 6×10^{-5} ergs). Many particles would therefore have to act simultaneously or their effects be additive; this would increase enormously the time required to produce a detectable quantity of helium. The second consideration is that four hydrogen atoms or possibly two hydrogen molecules must meet in order to form helium, and the energy must either be supplied at the moment of encounter, or they must be altered previously in such a way that they will associate on encounter and form helium. It is possible to calculate the probability of the occurrence of such a collision.

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* 'Jahrb. der Radioakt.,' p. 636 (1912).

The probability P_{2a} *of two atoms or molecules colliding* in a time dt is

$$\frac{T}{t}\,dt,$$

where T is the duration of the collision, t the time between two collisions.

But, according to kinetic theory,

$$t = \frac{1}{\pi\sigma^2 Npc},$$

σ = the diameter of an atom,
p = pressure,
N = number of atoms per unit volume at normal pressure and temperature,
c = mean velocity;

and

$$T = \frac{2f\sigma}{c/2},$$

where f is the fraction of the diameter to which distance the atoms interpenetrate; f will be a maximum when $f = \frac{1}{2}$.*

$$\therefore\quad P_{2a} = 4\pi Npf\sigma^3 dt.$$

Putting in values—
$N = 2{\cdot}75 \times 10^{19}$ molecules per cubic centimetre,
$p = 1$ mm.,
$f = \frac{1}{2}$,
$\sigma = 2 \times 10^{-8}$ cm.,

$$P_{2a} \leqq 1{\cdot}81 \times 10^{-6}\,dt.$$

The frequency of collision is $\pi\sigma^2 Npc$, *i.e.* $8{\cdot}7 \times 10^6$ times per second. The number of atoms per cubic centimetre at 1 mm. pressure is $3{\cdot}6 \times 10^{16}$ atoms. $\therefore$ total number of collisions in a tube of 100 c.c. is $1{\cdot}58 \times 10^{25}$ per second. The probability that during a collision lasting

$$\frac{2f\sigma}{c/2} = \frac{2 \times \frac{1}{2} \times 2 \times 10^{-8}}{1{\cdot}91 \times 10^8/2} = 2{\cdot}09 \times 10^{-13} \text{ secs. (at } 17^\circ \text{ C.)},$$

the colliding atoms will be struck by n other atoms is

$$2{\cdot}09 \times 10^{-13} \times (1{\cdot}81 \times 10^{-6})^n,$$

or for a fourfold collision

$$n = 2;$$

$$\therefore\quad P_{4a} = 6{\cdot}8 \times 10^{-25} dt,$$

and the number of collisions per second in a tube of 100 c.c. will become

$$(6{\cdot}8 \times 10^{-25})(1{\cdot}58 \times 10^{25}) = 10{\cdot}7 \text{ per sec.}$$

That helium can be produced by a fourfold collision of hydrogen atoms under certain special conditions is therefore quite out of the question, for there would have to be at least $7{\cdot}7 \times 10^8$ such collisions per second in order to produce a detectable quantity of helium in 10 hours.

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* J. H. Jeans, 'Dynamic Theory of Gases,' p. 205.

There remains the possibility that the helium might be produced from the collision of hydrogen molecules under certain conditions. It is difficult to see what those conditions in an electric discharge tube could be, other than the effect of an electron upon them. So it is necessary to calculate the chance of a collision of a cathode particle with the molecules of hydrogen.

The probability of an electron colliding with an atom or molecule would be $P_e = T/t' = T\nu$ where ν = number of times an electron collides with an atom per second.

$$\nu = \frac{a \times 3 \times 10^{10}}{10e} \cdot \frac{l}{\lambda} \cdot \frac{1}{n},$$

where a = current in ampères,
l = distance between electrodes,
λ = free path of electrons,
n = number of atoms in discharge tube.

The maximum value of T is σ/c', where
c' = velocity of electrons,
σ = diameter of atom.

But $c' = \sqrt{(2Ve\lambda/ml)}$, where V = potential between electrodes in E.S. units.

$$\therefore \quad T\nu = \frac{\sigma}{\sqrt{(2Ve\lambda/ml)}} \cdot \frac{a \times 3 \times 10^{10}}{10e} \cdot \frac{l}{\lambda} \cdot \frac{1}{n}.$$

But $\lambda = \dfrac{4\sqrt{2}}{\pi N p \sigma^2}$ and $n = Npv$, where v is volume;

therefore $$P_e = 3 \times 10^9 \cdot \frac{a}{e} \cdot \frac{l^{3/2}}{v} \cdot \frac{\pi^{3/2} N^{\frac{1}{2}} p^{\frac{1}{2}} \sigma^4}{\sqrt{(256\sqrt{2}\,Ve/m)}}.$$

Putting $a = 10^{-3}$ = 1 milliampère.
v = 100 c.c.,
l = 10 cm.,
p = 1 mm.,
$V = 10^4$ volts,

$$P_e = 4{\cdot}2 \times 10^{-18}\, dt.$$

The probability that an electron should strike a simple collision of two hydrogen molecules, which lasts 2×10^{-13} secs., is therefore $8{\cdot}4 \times 10^{-31}$, or as $1{\cdot}58 \times 10^{25}$ collisions take place per second, $1{\cdot}3 \times 10^{-5}$ atoms of helium might be formed per second, which would mean a detectable quantity in about 6×10^{11} years. Thus even a collision of an electron with two hydrogen molecules would be an inadequate explanation of the formation of the helium much more so the collision of four hydrogen atoms at a time, which would produce only *one atom* in about 10^{11} years. Likewise it could be shown that insufficient helium would be formed to detect in a reasonable period of time, even if the unlikely suggestion is assumed that the atoms or molecules are so altered by collision with the electrons, that when they subsequently collide with each other they might form helium atoms; for the probability of an electron colliding with an atom is small ($4 \cdot 2 \times 10^{-18}\, dt$), and even when such a collision does occur, the molecules which have encountered electrons must collide with each other.

The above calculations make it clear that the helium cannot arise from changes in the gases within the discharge tube, unless the conditions within a vacuum tube are very different from what they are taken to be and are such as to increase enormously the number of collisions of electrons, atoms, ions or molecules. This result is arrived at both from considerations of the energy needed to effect such a change and also from considerations of the possible mechanism producing such a change.

Next, let some disintegration process be assumed; could the helium be formed by the disintegration of the metallic electrodes or of the oxygen, silica, and other constituents of the glass or gases (oxygen, CO, etc.) in the discharge tube? The atomic weight of mercury is 200·6 and if the atoms were entirely split up into helium atoms, energy of the order of 10^{-3} ergs would be required per atom (this follows as before from Einstein's theory). For oxygen or carbon the quantity might be somewhat less than 10^{-5} ergs but for most elements it would be considerably more. The chances of finding in a discharge tube particles possessing sufficient energy to bring about such complete disintegration is exceedingly small; the α-particle possesses energy $1 \cdot 3 \times 10^{-5}$ ergs but even this does not seem to appreciably disintegrate the atoms it meets with.* However, there is no reason to suppose that the atoms must be completely disintegrated. It is quite conceivable that a partial disintegration and liberation of a helium atom from certain less stable atoms might arise under conditions of electric stress such as are obtained in a discharge tube. Such effects should be most likely to occur with the heaviest elements or possibly with rare earths or potassium.

From the above considerations it is more probable that the production of rare gases would arise from a process of disintegration than of association. Although it is not possible to make these calculations without certain assumptions which are not definitely established, it is unlikely that the orders of the above results would be greatly affected by future work: radioactivity affords evidence of the internal energy of an atom agreeing with that obtained by calculation; every gramme-atom of helium produced from radium releases about 10^{-19} ergs.

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* It is possible the α-particle does possess sufficient energy to disintegrate some of the atoms it encounters (see Ramsay and Cameron, 'Chem. Soc. Trans.,' vol. 91, p. 1605 (1907)).

Conclusion.

The attempt to produce rare gases (Ne and He) in accordance with the experiments of Collie and Patterson, by the passage of an electric discharge, has not been successful. Both from theoretical and experimental standpoints, it is held that if such a production has an origin other than from atmospheric contamination, the source must be looked for in some action on the solids which compose the discharge tube (electrodes or glass) rather than from the gases.

I am greatly indebted to my friend, Mr. F. A. Lindemann, for suggesting the method of calculating the probability of collision of electrons and atoms and of some of the samples of gas analysed. I have also to thank Prof. Nernst for his interest in these experiments carried out in his laboratory in Berlin. The experiments were conducted in continuation of work carried out with Sir William Ramsay on other lines but with somewhat similar apparatus, and to him and Prof. Collie I am grateful for the generous permission to publish the work.